



97934471.0

The  
Patent  
Office

PCT/EP 97 / 0 3 8 0 2

The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales  
NP9 1RH

REC'D 1 0 SEP 1997

WIPO PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

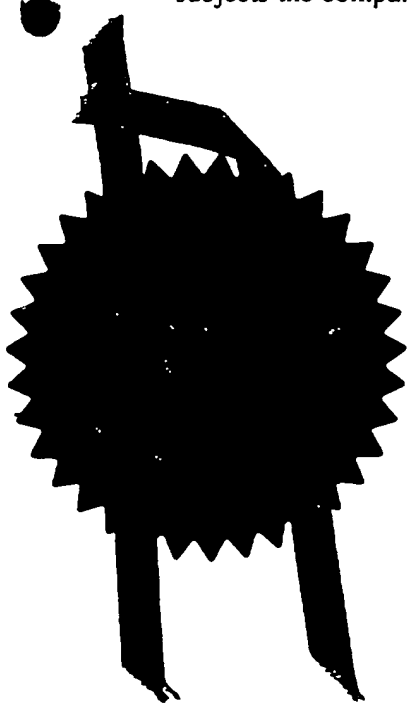
Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

PRIORITY DOCUMENT

Signed

Dated 13 August 1997

BEST AVAILABLE COPY





The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

# Request for grant of a patent

Read the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

1. Your reference	95.107	24 JUL 1996
2. Patent application number (The Patent Office will fill in this part)	<b>9615549.4</b>	
3. Full name, address and postcode of the or of each applicant ( <u>underline all surnames</u> )	Sofitech NV Rue de Stalle 142 B-1180 Brussels Belgium  Patents ADP number (if you know it)  If the applicant is a corporate body, give the country/state of its incorporation	
	Belgium  6546303003	
4. Title of the invention	AN ADDITIVE FOR INCREASING THE DENSITY OF A FLUID AND FLUID COMPRISING SUCH ADDITIVE	
5. Name of your agent (if you have one)	B D Stoole  "Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	
	Schlumberger plc 1st Floor 1 Kingsway London WC2B 6XH  Patents ADP number (if you know it)	
	1552006	
6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number	Country	Priority application number (if you know it)
		Date of filing (day / month / year)
7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing (day / month / year)
8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if: a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body See note (d))	Yes	

# Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document.

Continuation sheets of this form

Description	13
Claim(s)	2
Abstract	-
Drawing(s)	1

10. If you are also filing any of the following, state how many against each item.

Priority documents	-
Translations of priority documents	-
Statement of inventorship and right to grant of a patent (Patents Form 7/77)	1
Request for preliminary examination and search (Patents Form 9/77)	1
Request for substantive examination (Patents Form 10/77)	1
Any other documents (please specify)	-

11. ☒ We request the grant of a patent on the basis of this application.

*B D Stooile*

Signature

Date

23 July 1996

12. Name and daytime telephone number of person to contact in the United Kingdom

B D Stooile 0171 257 6394

## Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

## Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

## An Additive For Increasing The Density Of A Fluid

### And Fluid Comprising Such Additive

This invention relates to products which increase the density of wellbore fluids used during the construction or repair of oil, gas, injection, water or geothermal wells. The products of this invention may be used in any wellbore fluid such as drilling, cementing, completion, packing, work-over (repairing), stimulation, well killing, and spacer fluids.

One of the most important functions of a wellbore fluid is to contribute to the stability of the well bore, and control the flow of gas, oil or water from the pores of the formation in order to prevent, for example, the flow or blow out of formation fluids or the collapse of pressured earth formations. The column of fluid in the hole exerts a hydrostatic pressure proportional to the depth of the hole and the density of the fluid. High pressure formations may require a fluid with a specific gravity of up to 3.0.

A variety of materials are presently used to increase the density of wellbore fluids. These include dissolved salts such as sodium chloride, calcium chloride and calcium bromide. Alternatively powdered minerals such as barytes, calcite and hematite are added to a fluid to form a suspension of increased density. It is also known to utilise finely divided metal such as iron as a weight material. In this connection, PCT Patent Application WO85/05118 discloses a drilling fluid where the weight material includes iron/steel ball-shaped particles having a diameter less than 250 $\mu$ m and preferentially between 15 and 75 $\mu$ m. It has also been proposed to use calcium or iron carbonate (see for example US-A-4,217,229).

It is a requirement of wellbore fluids that the particles form a stable suspension, and do not readily settle out. A second requirement is that the suspension should exhibit a low viscosity in order to facilitate pumping and to minimise the generation of high pressures. Another requirement is that the wellbore fluid slurry should exhibit low filtration rates (fluid loss).

Conventional weighting agents such as powdered barytes ("barite") exhibit an average particle diameter ( $d_{50}$ ) in the range of 10-30 $\mu$ m. To suspend these materials adequately requires the addition of a gellant such as bentonite for water based fluids, or organically

modified bentonite for oil based fluids. A soluble polymer viscosifier such as xanthan gum may be also added to slow the rate of the sedimentation of the weighting agent. However, a penalty is paid in that as more gellant is added to increase the suspension stability, the fluid viscosity (plastic viscosity) increases undesirably resulting in reduced pumpability. This is  
5 obviously also the case if a viscosifier is used.

The sedimentation (or "sag") of particulate weighting agents becomes more critical in wellbores drilled at high angles from the vertical, in that sag of, for example, one inch can result in a continuous column of reduced density fluid along the upper portion of the wellbore wall. Such high angle wells are frequently drilled over large distances in order to  
10 access, for example, remote portions of an oil reservoir. In this case it becomes even more critical to minimise a drilling fluid's plastic viscosity in order to reduce the pressure losses over the borehole length.

This is no less important in deep high pressure wells where high density wellbore fluids are required. High viscosities can result in an increase in pressure at the bottom of the hole  
15 under pumping conditions. This increase in "Equivalent Circulating Density" can result in opening fractures in the formation, and serious losses of the wellbore fluid. Again, however, the stability of the suspension is important in order to maintain the hydrostatic head to avoid a blow out. The two objectives of low viscosity plus minimal sag of weighting material can be difficult to reconcile.

20 The need therefore exists for materials to increase fluid density which simultaneously provide improved suspension stability and less viscosity increase.

It is known that reduced particle sedimentation rates can be obtained by reducing the particle size used.

However, the conventional view in the drilling industry is that reducing the particle size  
25 causes an undesirable increase in viscosity. This is supposed to be caused by an increase in the surface area of the particles causing increased adsorption of water.

For example, "Drilling and Drilling Fluids" (Chilingarian G. V. and Vorabutor P. 1981), pages 441 - 444 states: "The difference in results (i.e. increase in plastic viscosity) when particle size is varied in a mud slurry is primarily due to magnitude of the surface area, which

determines the degree of adsorption (tying up) of water. More water is adsorbed with increasing area." Further it is also stated that "Viscosity considerations often will not permit the addition of any more of the colloidal solids necessary to control filtration, unless the total solids surface area is first reduced by removing a portion of the existing clays". The main thrust of the argument is that colloidal fines due to their nature of having a high surface area to volume ratio will adsorb significantly more water and so decrease the fluidity of the mud. This is why they and others have recommended that it is necessary in weighted particulate muds to remove the fine solids to reduce viscosity. The same argument or concept is presented in "Drilling Practices Manual" edited by Moore pages 185-189 (1986). Also, the API specification for barite as a drilling fluid additive limits the %w/w below 6 microns to 30% maximum in order to minimise viscosity increases.

It is therefore very surprising that the products of this invention, which comprise particles very finely ground to an average particle diameter ( $d_{50}$ ) of less than two microns, provide wellbore fluids of reduced plastic viscosity whilst greatly reducing sedimentation or sag.

The additives of this invention comprise dispersed solid colloidal particles with a weight average particle diameter ( $d_{50}$ ) of less than 2 microns and a defloculating agent or dispersant. The fine particle size will generate suspensions or slurries that will show a reduced tendency to sediment or sag, whilst the dispersant controlling the inter-particle interactions will produce lower rheological profiles. It is the combination of fine particle size and control of colloidal interactions that reconciles the two objectives of lower viscosity and minimal sag.

It is worth noting that small particles have already been used in drilling fluids but for a totally different purpose. Thus, EP-A-119 745 describes an ultra high density fluid for blow-out prevention comprised of water, a first and possibly second weighting agent and a gellant made of fine particles (average diameter from 0.5 to 10 $\mu$ m). The gelling agent particles are small enough to impart a good static gel strength to the fluid by virtue of the interparticle attractive forces. On the contrary, the present invention makes use of well dispersed particles : the interparticle forces tend to push away the other particles. If the concentration of small dispersed particles is sufficient, no gelling agent is needed.

According to the invention, a dispersant is added to the particulate weighting additive to allow it to find an acceptable conformation on the particle surface. This provides via a

manipulation of the colloidal interactions rheological control, tolerance to contaminants and enhanced fluid loss (filtration) properties. In the absence of the dispersant a concentrated slurry of these small particles, would be an unpumpable paste or gel. According to a preferred embodiment of the present invention, the dispersant is added during the grinding or comminution process. This provides an advantageous improvement in the state of dispersion of the particles compared to post addition of the dispersant to fine particles. The presence of the dispersant in the comminution process yields discrete particles which can form a more efficiently packed filter cake and so advantageously reduce filtration rates.

According to a preferred embodiment, the dispersant is chosen so as it provides the suitable colloidal inter-particle interaction mechanism to make it tolerant to a range of common wellbore contaminants, including salt saturated.

According to a preferred embodiment of the present invention, the weighting agent of the present invention is formed of particles that are composed of a material of specific gravity of at least 2.68. This allows wellbore fluids to be formulated to meet most density requirements yet have a particulate volume fraction low enough for the fluid to be pumpable.

A preferred embodiment of this invention is for the weight average particle diameter ( $d_{50}$ ) of the new weighting agent to be less than 1.5 micron. This will enhance the suspension's characteristics in terms of sedimentation or sag stability without the viscosity of the fluid increasing so as to make it unpumpable.

A method of comminuting a solid material to obtain material containing at least 60% by weight of particles smaller than  $2\mu\text{m}$  is known for example from British Patent Specification No 1,472,701 or No 1,599,632. The mineral in an aqueous suspension is mixed with a dispersing agent and then ground within an agitated fluidised bed of a particulate grinding medium for a time sufficient to provide the required particle size distribution. An important preferred embodiment aspect of the present invention is the presence of the dispersing agent in the step of "wet" grinding the mineral. This prevents new crystal surfaces formed during the comminution step from forming agglomerates which are not so readily broken down if they are subsequently treated with a dispersing agent.

The colloidal particles according the invention may be provided as a concentrated slurry either in an aqueous medium or an organic liquid. In the latter case, the organic liquid

should have a kinematic viscosity of less than 10 centistokes at 40 °C and, for safety reasons, a flash point of greater than 60 °C. Suitable organic liquids are for example diesel oil, mineral or white oils, n-alkanes or synthetic oils such as alpha-olefin oils, ester oils or poly(alpha-olefins).

- 5 Where the colloidal particles are provided in an aqueous medium, the dispersing agent may be, for example, a water soluble polymer of molecular weight of at least 2,000 Daltons. The polymer is a homopolymer or copolymer of any monomers selected from (but not limited to) the class comprising: acrylic acid, itaconic acid, maleic acid or anhydride, hydroxypropyl acrylate vinylsulphonic acid, acrylamido 2-propane sulphonic acid, acrylamide, styrene  
10 sulphonic acid, acrylic phosphate esters, methyl vinyl ether and vinyl acetate. The acid monomers may also be neutralised to a salt such as the sodium salt.

It is known that high molecular weight polymers act as flocculants by bridging between particles while low molecular weight polymers for instance (less than 10,000) act as deflocculants by creating overall negative charges.

- 15 It has been found that when the dispersing agent is added while grinding, intermediate molecular weight polymers (in the range 10,000 to 200,000 for example) may be used effectively. Intermediate molecular weight dispersing agents are advantageously less sensitive to contaminants such as salt and therefore are well adapted to wellbore fluids.

- Where the colloidal particles are provided in an organic medium, the dispersing agent may  
20 be selected for example among carboxylic acids of molecular weight of at least 150 such as oleic acid and polybasic fatty acids, alkylbenzene sulphonic acids, alkane sulphonic acids, linear alpha-olefin sulphonic acid or the alkaline earth metal salts of any of the above acids, phospholipids such as lecithin, synthetic polymers such as Hypermer OM-1 (trademark of ICI).

- 25 The colloidal particles comprise one or more materials selected from but not limited to barium sulphate (barite), calcium carbonate, dolomite, ilmenite, hematite or other iron ores, olivine, siderite, strontium sulphate. Normally the lowest wellbore fluid viscosity at any particular density is obtained by using the highest density colloidal particles. However other considerations may influence the choice of product such as cost, local availability and the  
30 power required for grinding.



Calcium carbonate and dolomite possess the advantage that residual solids or filter cake may be readily removed from a well by treatment with acids.

This invention has a surprising variety of applications in drilling fluids, cement, high density fluids and coiled tubing drilling fluids to highlight a few. The new particulate weighting agents have the ability to stabilise the laminar flow regime, and delay the onset of turbulence. It is possible to formulate fluids for several applications including coiled tubing drilling fluids, that will be able to be pumped faster before turbulence is encountered, so giving essentially lower pressure drops at equivalent flow rates. This ability to stabilise the laminar flow regime although surprising, is adequately demonstrated in heavy density muds of 20 pounds per gallon or higher. Such high density muds using conventional weighting agents with a weight average particle diameter of 10 to 30 microns would exhibit dilatancy with the concomitant increase in the pressure drops due to the turbulence generated. The ability of the new weighting agent to stabilise the flow regime even in the presence of a component of larger particles, means that high density fluids with acceptable rheology are feasible with lower pressure drops.

A further and unexpected application occurs in cement whereby the new weighting agent will generate slurries of a more controlled and lower rheology so allowing it to be pumped more freely into position. The reduced particle size will tend to have a less abrasive nature, whilst its suspension characteristics will reduce the free water and other suspension issues encountered when setting the cement. The high fraction of fines should also act as efficient fluid loss control agents, so preventing gas migration and producing stronger cements.

The fluids of the present invention may also be used in non-oilfield applications such as dense media separating fluid (to recover ore for example) or as a ship's ballast fluid.

The following examples are to illustrate the properties and performance of the wellbore fluids of the present invention though the invention is not limited to the specific embodiments showing these examples. All testing was conducted as per API RP 13 B where applicable. Mixing was performed on Silverson L2R or Hamilton Beach Mixers. The viscosity at various shear rates (RPM's) and other rheological properties were obtained using a Fann viscometer. Mud weight were checked using a standard mud scale or an analytical balance. Fluid loss was measured with a standard API fluid loss cell.

In expressing a metric equivalent, the following U.S. to metric conversion factors are used :

1 gal = 3.785 litres ; 1 lb. = 0.454 kg ; 1 lb./gal (ppg)=0.1198 g/cm<sup>3</sup> ; 1 bbl=42 gal ;  
1 lb./bbl (ppb)=2.835 kg/m<sup>3</sup> ; 1 lb/100ft<sup>2</sup>=0.4788 Pa.

These tests have been carried out with different grades of barite : a standard grade of API  
5 barite, having a weight average particle diameter ( $D_{50}$ ) of about 20  $\mu\text{m}$  ; a commercial barite  
(M) made by milling/grinding barite whilst in the dry state, with an average size of 3  $\mu\text{m}$ -5  $\mu\text{m}$   
and colloidal barite according the present invention (with a  $D_{50}$  from 0.5  $\mu\text{m}$  to 1.5  $\mu\text{m}$ ),  
with a dispersant included during the "wet" grinding process. The corresponding particle  
size distributions are shown figure 1. The dispersant is IDSPERSE XT (Mark of  
10 Schlumberger), an anionic acrylic ter-polymer of molecular weight in the range  
40,000-120,000 with carboxylate and other functional groups. This preferred polymer is  
advantageously stable at temperature up to 200 °C, tolerant to a broad range of  
contaminant, gives good filtration properties and do not readily desorb off the particle  
surface.

15

### Example 1

22 ppg fluids based on barium sulphate and water were prepared using standard barite and  
colloidal barite according to the invention. The 22ppg slurry of API grade barite and water  
was made with no gelling agent to control the inter-particle interactions (Fluid #1). Fluid #2  
20 is also based on standard barite but with a post-addition of two pounds per barrel  
IDSPERSE XT. Fluid #3 is 100% new weighting agent with 67% w/w of particles below 1  
micron in size and at least 90% less than 2 microns. The results are provided in table I.

**Table I**

#	Viscosity at various shear rates (rpm of agitation) : Dial reading or "Fann Units" for :						Plastic Viscosity	Yield Point
	600 rpm	300 rpm	200 rpm	100 rpm	6 rpm	3 rpm	mPa.s	lb/100ft <sup>2</sup> (Pascals)
1	250	160	124	92	25	16	90	70 (34)
2	265	105	64	26	1	1	160	-55 (-26)
3	65	38	27	17	3	2	27	11 (5)

For Fluid #1 the viscosity is very high and the slurry was observed to filter very rapidly. (If further materials were added to reduce the fluid loss, the viscosity would increase yet further). This system sags significantly over one hour giving substantial free water (ca. 10% of original volume).

Post addition of two pounds per barrel of IDSPERSE XT to this system (Fluid #2) reduces the low shear rate viscosity by controlling the inter-particle interactions. However due to the particle concentration and average particle size the fluid exhibits dilatancy which is indicated by the high plastic viscosity and negative yield point. This has considerable consequences on the pressure drops for these fluids whilst pumping. The fluid #2 sags immediately on standing.

By contrast, Fluid #3 exhibits an excellent, low, plastic viscosity. The presence of the dispersing polymer controls the inter-particle interactions, so making fluid #3 pumpable and not a gel. Also the much lower average particle size has stabilised the flow regime and is now laminar at  $1000 \text{ s}^{-1}$  demonstrated by the low plastic viscosity and positive yield point.

### Example 2

Experiments were conducted to examine the effect of the post addition of the chosen polymer dispersant to a slurry comprising weighting agents of the same colloidal particle size. A milled barite ( $D_{50} \sim 4\mu\text{m}$ ) and a comminuted Calcium carbonate (70% by weight of the particles of less than  $2\mu\text{m}$ ) were selected, both of which are of similar particle size to the invention related herein. The slurries were prepared at an equivalent particle volume fraction of 0.282. See table II.

The rheologies were measured at 120° F, thereafter an addition of 6ppb IDSPERSE XT was made. The rheologies of the subsequent slurries were finally measured at 120°F (see table III) with additional API fluid loss test.

5 **Table II**

#	Material	Dispersant	Density (ppg)	Volume Fraction	wt/wt
4	New Barite	while grinding	16.0	0.282	0.625
5	Milled Barite	none	16.0	0.282	0.625
6	Milled Barite	post-addition	16.0	0.282	0.625
7	Calcium Carbonate	none	12.4	0.282	0.518
8	Calcium Carbonate	post-addition	12.4	0.282	0.518

**Table III**

#	Viscosity at various shear rates (rpm of agitation) : Dial reading or "Fann Units" for :						Plastic Viscosity	Yield Point	API Fluid Loss
	600 rpm	300 rpm	200 rpm	100 rpm	6 rpm	3 rpm	mPa.s	lb/100ft <sup>2</sup>	
4	12	6	4	2			6	0	11
5	os	os	os	os	os	os			
6	12	6	4	2			6	0	total <sup>1</sup>
7	os	os	260	221	88	78			
8	12	6	4	3	1	1	6	0	total <sup>2</sup>

1 - total fluid loss in 26 minutes

2 - total fluid loss in 20 minutes

- 10 No filtration control is gained from post addition of the polymer as revealed by the total fluid loss in the API test.

### **Example 3**

- This test was carried out to show the feasibility of 24 ppg slurries (0.577 Volume fraction). Each fluid contained the following components e.g. Fresh Water 135.4 g, Total Barite 861.0g, IDSPERSE XT 18.0 g. The barite component was varied in composition according to the following table.
- 15

**Table IV**

#	API grade Barite (%)	Colloidal Barite (%)
9	100	0
10	90	10
11	80	20
12	75	25
13	60	40
14	0	100

**Table V**

#	Viscosity at various shear rates (rpm of agitation) : Dial reading or "Fann Units" for :									Plastic Viscosity	Yield Point
	600	300	200	117	100	59	30	6	3	mPa.s	lb/100ft <sup>2</sup> (Pascals)
9	*os	285	157	66	56	26	10	3	2		
10	245	109	67	35	16	13	7	3	2	136	-27 (-13)
11	171	78	50	28	23	10	7	3	2	93	-15 (-7)
12	115	55	36	19	17	8	5	3	2	60	-5 (-2)
13	98	49	34	21	20	14	10	4	3	49	0
14	165	84	58	37	32	22	18	5	3	81	3 (-1.5)

\* os = off-scale

- 5 The results provided table V show that API grade barite due to its particle size and the high volume fraction required to achieved high mud weights exhibit dilatancy i.e. high plastic and apparent viscosity and negative yield values.

- 10 Introduction of fine grade materials tends to stabilise the flow regime keep it laminar at higher shear rates : plastic viscosity decreases markedly and yield point changes from negative to positive. No significant increase in low-shear rate viscosity (@ 3 rpm) is caused by the colloidal barite.

These results show that the colloidal weight material of this invention may advantageously be used in conjunction with conventional API barite.

**Example 4**

An eighteen (18) pound per gallon slurry of weighting agent according the present invention was formulated and subsequently contaminated with a range of common contaminants and hot rolled at 300 °F (148.9 °C). The rheological results of before (BHR) and after hot rolling (AHR) are presented below. The system shows excellent resistance to contaminants, low controllable rheology and gives fluid loss control under a standard API mud test as shown in following table VI : An equivalent set of fluids were prepared using API conventional barite without the polymer coating as a direct comparison of the two particle types. (Table VII)

**Table VI (New barite)**

	Viscosity (Fann Units) at various shear rates (rpm of agitation :						PV	YP	Fluid loss
	600	300	200	100	6	3	mPa.s	lb/100ft <sup>2</sup> (Pascals)	ml
no contaminant BHR	21	11	8	4	1	1	10	1(0.5)	
no contaminant AHR	18	10	7	4	1	1	8	2(1)	5.0
+80ppb NaCl BHR	41	23	16	10	2	1	18	5(2.5)	
+80ppb NaCl AHR	26	14	10	6	1	1	12	2(1)	16
+30ppb OCMA <sup>1</sup> BHR	38	22	15	9	2	1	16	6(3)	
+30ppb OCMA AHR	26	14	10	6	1	1	12	2(1)	6.8
+5ppb Lime BHR	15	7	5	3	1	1	8	-1(-0.5)	
+5ppb Lime AHR	10	5	4	2	1	1	5	0	6.4

<sup>1</sup> OCMA = Ocma clay, a fine particle ball clay commonly used to replicate drilled solids contamination acquired from shale sediments during drilling

**Table VII( Conventional API Barite)**

	Viscosity (Fann Units) at various shear rates (rpm of agitation :						PV	YP	Fluid loss
	600	300	200	100	6	3	mPa.s	lb/100ft <sup>2</sup> (Pascals)	ml
no contaminant BHR	22	10	6	3	1	1	12	-2	
no contaminant AHR	40	24	19	11	5	4	16	8	Total <sup>1</sup>
+80ppb NaCl BHR	27	13	10	6	2	1	14	-1	
+80ppb NaCl AHR	25	16	9	8	1	1	9	7	Total <sup>1</sup>
+30ppb OCMA BHR	69	55	49	43	31	26	14	31	

+30ppb OCMA AHR	51	36	31	25	18	16	15	21	Total <sup>2</sup>
+5ppb Lime BHR	26	14	10	6	2	1	12	2	
+5ppb Lime AHR	26	14	10	6	1	1	12	2	Total <sup>1</sup>

1 - Total fluid loss within 30 seconds

2 - Total fluid loss within 5 minutes.

A comparison of the two sets of data show that the weighting agent according the present invention has considerable fluid loss control properties when compared to the API barite.

- 5 The API barite also shows sensitivity to drilled solids contamination whereas the new barite system is more tolerant.

### Example 5

An experiment was conducted to demonstrate the ability of the new weighting agent to formulate drilling muds with densities above 20 pound per gallon.

- 10 Two twenty two pound per gallon mud systems were formulated, the weighting agents comprised a blend of 35% w/w new barite weighting agent with 65% w/w API grade Barite (Fluid #1) weighting agent and 100% API grade barite (fluid #2), both with 11.5 pound per barrel STAPLEX 500 (mark of Schlumberger, shale stabiliser), 2 pound per barrel IDCAP (mark of Schlumberger, shale inhibitor), and 3.5 pound per barrel KCl. The other additives
- 15 provide inhibition to the drilling fluid, but here demonstrate the capacity of the new formulation to cope with any subsequent polymer additions. The fluid was hot rolled to 200 °F (93.3 °C). Results are provided in table VIII.

Table VIII

	Viscosity (Fann Units) at various shear rates (rpm of agitation :						PV	Yield Point	Fluid loss
	600	300	200	100	6	3	mPa.s	lb/100ft <sup>2</sup> (Pascals)	ml
Before Hot Rolling (#1)	110	58	46	30	9	8	52	6 (2.9)	
After Hot Rolling(#1)	123	70	52	30	9	8	53	17 (8.1)	8.0
Before Hot Rolling (#2)	270	103	55	23	3	2	167	-64 (-32)	
After Hot rolling(#2)	os	177	110	47	7	5			12.0

os : off scale

The 100% API grade barite has very high plastic viscosity and is in fact turbulent as demonstrated by the negative yield point. after hot rolling the rheology is so high it is off scale.

### Example 6

- 5 This experiment demonstrates the ability of the new weighting agent to low viscosity fluids. The weighting agent is 100% colloidal barite according the present invention. Fluid #15 is based on a pseudo oil (Ultidril, Mark of Schlumberger, a linear alpha olefin having 14 to 16 carbon atoms). Fluid #15 is a water based mud and includes a viscosifier (0.5 ppb IDVIS, Mark of Schlumberger, a pure xanthan gum polymer) and a fluid loss control agent (6.6 ppb
- 10 IDFLO, Mark of Schlumberger). Fluid #15 was hot rolled at 200 °F (93.3 °C), fluid #16 at 250 °F (121.1 °C). After hot rolling results are shown table IX.

Table IX

	Viscosity (Fann Units) at various shear rates (rpm of agitation :						PV	Gels <sup>1</sup>	Yield Point
	600	300	200	100	6	3			
							mPa.s	lbs/100ft <sup>2</sup> (Pascals)	lbs/100ft <sup>2</sup> (Pascals)
#15 : 13.6 ppg	39	27	23	17	6	5	12	7/11	15
#16 : 14 ppg	53	36	27	17	6	5	17	5/-	19

- 15 <sup>1</sup> A measure of the gelling and suspending characteristics of the fluid, determined at 10 sec/10 min using a Fann viscosimeter.

Even though the formulation was not optimized, this test makes clear that the new weighting agent provides a way to formulate brine analogues fluids useful for slimhole applications or coiled tubing drilling fluids. The rheology profile is improved by the addition of colloidal particles.



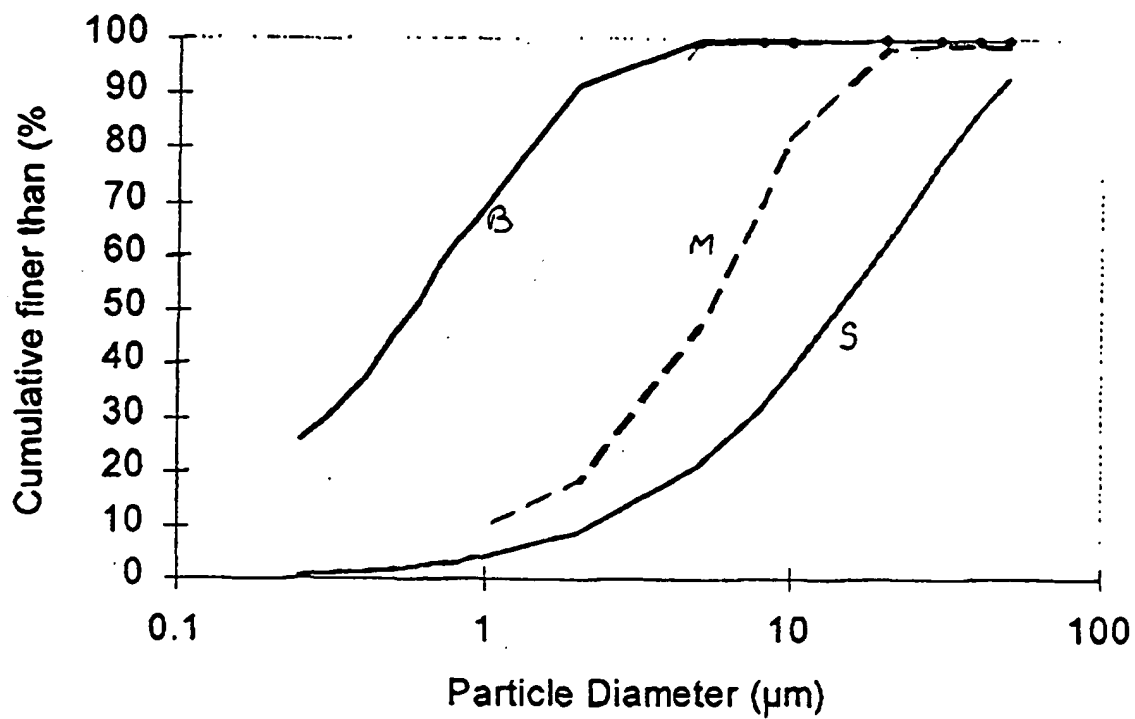
## Claims ---

1. An additive for increasing the density of a fluid wherein the additive comprises solid colloidal particles of weight average particle diameter ( $D_{50}$ ) of less than 2 microns, the particles being deflocculated by the action of a dispersant.
- 5 2. An additive according to claim 1 wherein the dispersant is incorporated into the additive during the process of grinding or comminution of the particles to the specified particle size.
3. An additive according to either preceding claim wherein the colloidal particles are composed of a material of specific gravity of at least 2.68.
- 10 4. An additive according to any preceding claim wherein the colloidal particles have a  $D_{50}$  of less than 1.5 micron diameter.
5. An additive according to any preceding claim wherein the colloidal particles comprise one or more materials selected from barium sulphate, calcium carbonate, dolomite, ilmenite, hematite or other iron ores, olivine, siderite, strontium sulphate.
- 15 6. An additive according to any preceding claim wherein the colloidal particles are ground, stored, transported, and added to the wellbore fluid in a slurry form in a suitable liquid medium.
7. An additive according to claim 6 wherein the liquid medium is an aqueous phase.
8. An additive according to claim 6 wherein the liquid medium is an organic liquid of  
20 kinematic viscosity less than 10 centistokes at 40 °C and of flash point of greater than 60 °C.
9. An additive according to claim 7 wherein the aqueous slurry of colloidal particles contains a dispersant comprising a water soluble polymer of molecular weight of at least 2,000 Daltons and wherein the polymer is a homopolymer or copolymer of any  
25 monomers selected from (but not limited to) the class comprising: acrylic acid, itaconic acid, maleic acid or anhydride, hydroxypropyl acrylate vinylsulphonic acid, acrylamido 2 propane sulphonic acid, acrylamide, styrene sulphonic acid, acrylic phosphate esters,

methyl vinyl ether and vinyl acetate, and wherein the acid monomers may also be neutralised to a salt such as the sodium salt.

10. An additive according to claim 8 wherein the organic liquid slurry of colloidal particles contains a dispersant selected from carboxylic acids of molecular weight of at least 150 such as oleic acid and polybasic fatty acids, alkylbenzene sulphonic acids, alkane sulphonic acids, linear alpha olefin sulphonic acid or the alkaline earth metal salts of any of the above acids, phospholipids such as lecithin.
11. An additive according to any preceding claim wherein the colloidal particles are formed by grinding a suitable feedstock in an agitated fluidised bed of a particulate grinding material.
12. An additive according to any preceding claim wherein the wellbore fluid is any one of the class including; drilling fluid, cement slurry, completion fluid, workover fluid, slimhole drilling fluid, packer fluid, spacer fluid, stimulation fluid, testing fluid, kill fluid, coiled tubing fluid.
13. Use of the additive according to any preceding claim in a wellbore fluid used for constructing or treating oil, gas, water, geothermal wells and the like.
14. Use of the additive according to any of claims 1 to 12 in a dense media separating fluid or in a ship's ballast fluid.

# Barite Distributions



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

### **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

### **IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**